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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the phthalocyanine system constituent used for the photo conductor (henceforth a digital photo conductor) which reacts in digital one to the optical input used in the electro photography industry.

[0002]

[Description of the Prior Art]From the former, to an electrophotographing system and the photo conductor used for it. The thing near a simple photo conductor was used, the so-called photo conductor of the Carlsson method was left, and the photosensitive layer of the amorphous state of an Se system, the amorphous layer of silicon, the binding layer of ZnO which made similar with the amorphous layer

of Se and was made, etc. have been used. Although the so-called photosensitive layer of the functional discrete type which uses an organic semiconductor has also come to be used recently, since the personal history has developed based on an analog concept, any electrophotographying system uses the material chosen so that the photoelectric current of the amount of input light and a similar quantity might flow.

[0003]In order for electrophotographic technology and online-communications art to join together in recent years, the printer and the facsimile have changed to an electro photography recording method rapidly. As for an electro photography recording method, a digital recording system came to be desired rather than the conventional analog recording method for PPC in connection with this.

Although the concept of the photo conductor for digital optical inputs is expressed to JP,H1-169454,A, the material which can be used for this photo conductor is not specifically described.

[0004]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the phthalocyanine system photoconductivity constituent which is needed for Data Processing Division of computer out, the computer machine which carries out digital decomposition and processes a picture, etc. and which reacts in digital one to input light.

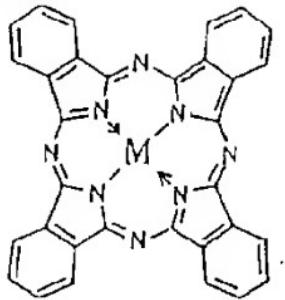
[0005]

[Means for Solving the Problem]This invention is a

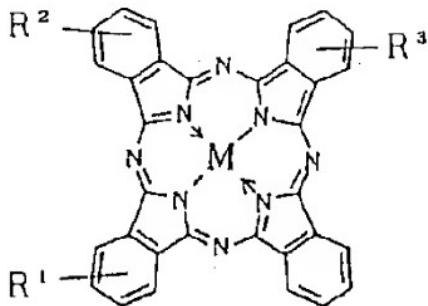
phthalocyanine system photoconductivity constituent which mixes a compound shown by 0.001 - 5 weight section and a formula (3) in a compound shown by a formula (2) to compound 100 weight section shown by a formula (1) with composition ratio of 0.01 - 10 weight section, and is obtained by carrying out milling processing.

[0006]

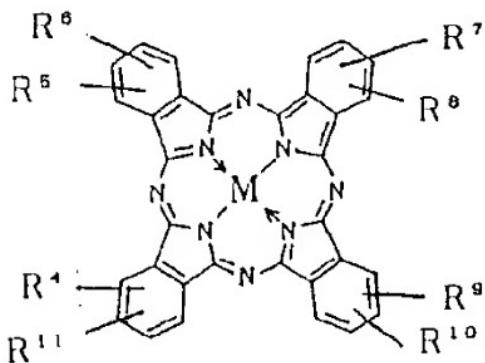
[Formula 2]



(1)



(2)



(3)

[0007](Although M expresses a hydrogen atom or phthalocyanine, a covalent bond, the atom that may be

coordinated, or a compound among the above-mentioned formula and R¹ - R³ express a hydrogen atom or a halogen atom, and a nitro group, at least one is a halogen atom or a nitro group.) Although R⁴ - R¹¹ are the same or different and a hydrogen atom, a halogen atom, or an electronic suction nature group is expressed, at least four are a halogen atom or an electronic suction nature group.

[0008]As M in a phthalocyanine ring of a formula (1), a formula (2), and a formula (3), For example, an oxide or a halogenide of a hydrogen atom, magnesium, calcium, zinc, aluminum, titanium, tin, lead, vanadium, iron, cobalt, nickel, copper, silicon, or these metal is mentioned.

Preferably, it is a hydrogen atom, copper, cobalt, lead, nickel, titanyl, vanadyl, and magnesium, and they are a hydrogen atom, copper, titanyl, vanadyl, and magnesium still more preferably. a desirable compound among compounds of a formula (2) of this invention -- inside of R¹ - R³ -- one -- or one is a halogen atom or a nitro group still more preferably two. As a halogen atom, bromine, fluoride, and chlorine are chlorine desirable still more preferably.

[0009]A compound of a formula (2) is 0.001 - 5 weight section to compound 100 weight section of a formula (1), and the mixing ratio of a phthalocyanine system mixture which mixed a compound of a formula (1) of this invention and a compound of a formula (2) is 0.001 - 3 weight section preferably. Although the phthalocyanine system mixture can also mix and obtain a compound of a formula (1), and a compound of a formula (2), As a general manufacturing

method, It is manufactured also by making phthalocyanine form using the above-mentioned raw material compound (it is considered as the compound B below) replaced by a raw material compound (it is considered as compound A below), a halogen atom, or a nitro group which can form a phthalocyanine ring used in the case of phthalocyanine composition. A presentation rate of compound A and the compound B is 0.001 to compound B5 weight section to compound-A 100 weight section, and is 0.001 to 3 weight section preferably.

[0010]If compound A and the compound B are the above-mentioned presentation rates, a phthalocyanine system mixture, By heating and stirring nitrogen donors, such as a catalyst, metal salt or a hydrogen donor, and urea, in an inactive solvent, when compounding an organic compound and phthalocyanine which what kind of process may be sufficient as, for example, can form a phthalocyanine ring, it is obtained as a required auxiliary compound.

[0011]As an organic compound which can form a phthalocyanine ring, there are phthalic acid, phthalic anhydride, phthalamide, phthalic acid monoamide, a phthalimide, orthocyanobenzamide, phtalo dinitrile, amino imino ISOINDO renin, PORIAMINOIMINO ISOINDORENIN, etc. In obtaining non-metal phthalocyanines and obtaining metal phthalocyanines using hydrogen donors, such as cyclohexylamine, it compounds a phthalocyanine ring by using metal salt like a cuprous chloride. In the case of an organic compound lacking in a

nitrogen atom required to form an aza porphin core like phthalic acid, a phthalocyanine ring is obtained by heating and stirring a catalyst of ammonium molybdate, and a nitrogen donor like urea.

[0012]As a substituent of a compound of a formula (3) of this invention, A halogen atom or an electron withdrawing group is used, a nitro group, a cyano group, a sulfonic group, a carboxyl group, etc. are mentioned as an electron withdrawing group, a nitro group, a cyano group, and a halogen atom are preferred as a substituent, and a nitro group and a halogen atom are still more preferred. As the number of substituents of a halogen atom or an electron withdrawing group, 4-8 pieces are preferred and 4-6 pieces are still more preferred.

[0013]A compound of a formula (3) is 0.01 - 10 weight section to 100 weight sections of a compound of formula (I), and a presentation rate of a phthalocyanine system mixture and a compound of a formula (3) is 0.01 - 5 weight section preferably.

[0014]As a manufacturing method of a phthalocyanine system constituent of this invention, it is manufactured by carrying out milling processing of a phthalocyanine system mixture and the compound of a formula (3). As for time, temperature performs a phthalocyanine system mixture of the above-mentioned rate, and a compound of a formula (3) from a room temperature to 200 ** in 0.5 - 200 hours, using mechanical mixers, such as a ball mill, attritor, a sand mill, and a kneader, as milling processing of this invention.

[0015]In milling processing of this invention, processings (the acid pasting method, acid slurry method, etc.) beforehand called paints-ization in a phthalocyanine system mixture of the above-mentioned rate and a compound of a formula (3) are performed, and what was made into mixed stock can be used.

[0016]In order to use a phthalocyanine system constituent of this invention as a photo conductor for electro photography, kneading dispersion machines, such as a ball mill and attritor, are made to distribute uniformly, it applies on a conductive substrate, and a photosensitive layer is made to form with binder resin, a solvent, etc.

[0017]That is, this photoconductivity constituent is applied on conductive substrates, such as an aluminum plate usually used for an electrophotographic photoreceptor, paper which carried out electric conduction processing, and a plastic, and a photosensitive layer is made to form. If necessary, a solvent will be added to a photoconductivity constituent and viscosity will be adjusted, and it applies with coating methods, such as an air doctor coating-machine, braid coating-machine, rod coating-machine, reverse coating-machine, spray-coater, hot coating-machine, and squeeze coating machine and a photogravure coating machine, and a tunic is made to form. After spreading, it dries suitably so that it can have electrification potential sufficient as a photosensitive layer.

[0018]As binder resin, melamine resin, an epoxy resin, a fluoro-resin, silicone resin, Polyurethane resin, polyester

resin, alkyd resin, an acrylic resin, Binder resin in which volume resistivity, such as xylene resin, polyvinyl chloride acetate copolymer resin, polycarbonate resin, and a fibrin derivative, has the insulation more than 10^7 omegacm, such as bending resin or a polyvinyl carbazole, is mentioned.

[0019]Resin / photoconductivity material is one or more in a weight ratio, for example, an electrophotographic photoreceptor obtained by a method of this invention has many resin amounts compared with a case of a photo conductor using a zinc oxide, and its physical intensity of a tunic is high, and it is a photo conductor which is rich in flexibility. It has the practically outstanding feature, such as manufacture with few problems of toxicity with little aging whose moisture resistance is [with a large adhesive property with a conductive substrate] good being easy for a photo conductor for electro photography of this invention, it being cheap, and being.

[0020]In the case of the conventional photo conductor, a photo conductor for electro photography using a phthalocyanine system constituent of this invention obtained as mentioned above (it is hereafter considered as a photo conductor of this invention) is compared, and since how to flow through specific photoelectric current is adopted, it can be used as a digital photo conductor.

[0021]That is, to photoelectric current of quantity according to the amount of input light flowing through the conventional photo conductor, photoelectric current does not flow, or a photo conductor of this invention is little very

much, and immediately after a certain amount of input light exceeds the light volume, photoelectric current flows through it rapidly [from] to it. The above-mentioned thing of a digital recording is [the light sensitivity characteristic of a photo conductor used for this recording method] preferred in order to express picture gradation with a dot area. Because, since distribution or halo of light volume of the spot itself are not theoretically avoided even if it modulates laser spot correctly by an optical system, It is because a dot pattern changes and it becomes a cause of fogging as a noise by light volume change in the conventional photo conductor which gathers gradually change of light energy (the amount of input light). Therefore, phthalocyanine system constituents of this invention are photosensitive materials advantageous to a digital photo conductor. Hereafter, working example explains this invention. In inside of a formula "part", a weight section is shown.

[0022]

[Example]

0.02 copy of working example 14-chlorophthalic anhydride, 18 copies of phthalic anhydride, After it filtered the mixture obtained by heating and stirring 31 copies of urea, 5.1 copies of cupric chlorides, 0.2 copy of ammonium molybdate, and 150 copies of nitrobenzene with the reaction temperature of 190 ** for 5 hours and methanol washed enough, in 1,000 copies of 1N hydrochloric acid aqueous solutions, it boiled for 1 hour and filtered at the

time of heat. After washing until the filtrate became neutrality with sufficient water, it boiled in 1,000 copies of 1N sodium hydroxide solution for 1 hour. It filtered promptly at the time of heat, and it washed until the filtrate became neutrality with sufficient water. It dried at 110 ** and 14 copies of copper-phthalocyanine system mixtures (A) were obtained. 30 time processings of 0.2 copy of tetrannitrocopper phthalocyanine were carried out to ten copies of this copper-phthalocyanine system mixture (A) at 80 ** by ball milling, and 9.5 copies of phthalocyanine system constituents were obtained.

[0023]Ten copies of copper-phthalocyanine system mixtures (A) and 0.2 copy of tetrannitrocopper phthalocyanine which were obtained in working example 2 working example 1 were dissolved in 100 copies of sulfuric acid. Subsequently, after dropping this acid solution into 110 copies of water, and ice water of 410 copies of ice and making it reprecipitate, it filtered, and it washed until the filtrate became neutrality with sufficient water. 30 time processings of the mixture obtained by drying at 110 ** were carried out at 80 ** by ball milling like working example 1, and 9.8 copies of phthalocyanine system constituents were obtained.

[0024]By the sand mill, 150 time processings of ten copies of copper-phthalocyanine system mixtures (A) and 0.1 copy of octachlorocopper phthalocyanine which were obtained in working example 3 working example 1 were carried out at the room temperature, and 9.3 copies of phthalocyanine

system constituents were obtained.

[0025]0.18 copy of working example 44-nitrophthalic anhydride, 18 copies of phthalic anhydride, After heating and stirring 31 copies of urea, 5.1 copies of cupric chlorides, 0.2 copy of ammonium molybdate, and the mixture of 150 copies of alkylbenzenes with the reaction temperature of 190 ** for 5 hours, 18 copies of copper-phthalocyanine system mixtures (B) were obtained by the same operation as working example 1. Ten copies of this mixture (B) and 0.3 copy of tetranitrocopper phthalocyanine were processed with sulfuric acid like working example 2. Then, with the ball mill, 30 time processings were carried out at 80 **, and 9.3 copies of phthalocyanine system constituents were obtained.

[0026]0.8 copy of working example 54-chlorophthalonitrile, 29 copies of phthalonitriles, After carrying out acid treatment of ten copies of non-metal-phthalocyanines system mixtures (C) and 0.1 copy of tetranitro non-metal phthalocyanines which were obtained from three copies of cyclohexylamines, and 100 copies of nitrobenzene by the same operation as working example 1 like working example 2, With the ball mill, 30 time processings were carried out at 60 **, and 9.6 copies of phthalocyanine system constituents were obtained.

[0027]After carrying out acid treatment of ten copies of phthalocyanine system mixtures (C) and 0.2 copy of tetranitro non-metal phthalocyanines which were obtained in working example 6 working example 5 like working

example 2, by attritor, 70 time processings were carried out at the room temperature, and 9.3 copies of phthalocyanine system constituents were obtained.

[0028]The rate of each compound of the phthalocyanine system constituent obtained in above-mentioned working example 1-6 was searched for by the analytical curve method which used the parent peak intensity of FD-mass spectrum. The rate of the compound of the formula (2) to 100 copies of compounds of the formula (1) in a class product and a formula (3) was shown in the 1st table.

[0029]

[Table 1]

第1表

実施例	式(1)	式(2)	式(3)
1	1 0 0	0. 1	2. 0
2	1 0 0	0. 1	2. 0
3	1 0 0	0. 1	1. 0
4	1 0 0	0. 9	2. 5
5	1 0 0	0. 5	1. 0
6	1 0 0	0. 5	2. 0

[0030]The phthalocyanine system constituent which is beyond the example of an examination and was produced by making was used as the electrophotographic photoreceptor as follows. 0.8 copy of phthalocyanine system constituent -- a polyester resin solution (Alma textile.) It put into the constituent which consists of P645, Mitsui Toatsu

Chemicals, Inc. make 2.8 copy, one copy of melamine resin (Cauvin, 20HS, Mitsui Toatsu Chemicals, Inc. make), and 14 copies of cyclohexanones with 30 copies of glass beads, the paint mixer distributed for 4 hours, and photo conductor coating liquid was obtained. Next, on 90-micron-thick aluminium foil, this photo conductor coating liquid was applied so that dry membrane thickness might be 15 microns, and it was neglected at 200 ** for 3 hours, and the electrophotographic photoreceptor was obtained.

[0031]The obtained photo conductor evaluated the light sensitivity characteristic using the photo conductor evaluation system (made in [JIEN tech company] Cynthia 55). +Corona electrical charging was carried out on the voltage of 6.0 kV, and the surface potential of the photo conductor made time (second) of the folding point to which it falls rapidly dark decay time. The optical characteristic was defined as follows. The photo conductor which electrified the monochromatic light which is 780 nm from which light intensity differed was irradiated respectively, the attenuating light curve (surface potential versus irradiation time) to each light intensity was measured respectively, and the surface potential after the fixed time exposure (here 0.5 second) of the curve was respectively plotted to light energy.

[0032]The minimum light energy was made into E_2 among the light energies to which the greatest light energy can reduce E_1 and surface potential to a rest potential grade (about 30V) among the light energies which can maintain

surface potential to the almost same grade as initial electrification. It can become a photo conductor which reacts so in [that photosensitivity is so good that E_1 is small and difference ΔE of $E_2 - E_1$ is small] digital one. In this appraisal method, below by 20 microJ/cm^2 , a digital photo conductor is possible for ΔE , and it can consider more than it to be an analog photo conductor. The following comparative example was also doubled and evaluated for comparison.

[0033]Phthalocyanine which obtained comparative example 1 80 ** of unplaced copper phthalocyanines by carrying out 30 time processings with the ball mill like working example 1.

[0034]The phthalocyanine system constituent which obtained comparative example 2 ten copies of unplaced copper phthalocyanines, and 0.2 copy of tetrannitrocopper phthalocyanine by carrying out 150 time processings at a room temperature by the sand mill like working example 3.

[0035]Ten copies of copper-phthalocyanine system mixtures (A) and 0.2 copy of tetrannitrocopper phthalocyanine which were obtained in comparative example 3 working example 1 were dissolved in 100 copies of sulfuric acid. Subsequently, the phthalocyanine system constituent which was filtered, was washed until the filtrate became neutrality with sufficient water, and was dried and obtained at 110 ** after dropping this acid solution into 110 copies of water, and ice water of 410 copies of ice and making it reprecipitate.

[0036]The result of having evaluated working example 1-6 and the comparative examples 1, 2, and 3 in accordance with the above-mentioned appraisal method was shown in the 2nd table. Dark decay time of the sample of the comparative examples 1 and 2 was made into time (second) to set initial surface potential to one half in order not to show a folding point.

[0037]

[Table 2]

第2表

	暗減衰時間 (秒)	E_1 ($\mu J/cm^2$)	E_2 ($\mu J/cm^2$)	$\Delta E (E_2 - E_1)$ ($\mu J/cm^2$)	残留電位 (V)
実 1	120	2.0	5.0	3.0	20
	2	45	2.0	4.5	25
施 3	85	4.5	12	7.5	30
	4	70	2.0	5.0	25
例 5	40	0.9	1.9	1.0	20
	6	60	1.0	2.5	20
比 1	200以上	0.4	210	209.6	320
較 2	50	0.1	64.5	64.4	30
例 3	20	5.0	30.0	25.0	20

[0038]

[Effect of the Invention]The phthalocyanine system constituent of this invention is the photosensitive layer which carried out lamination with the insulating binder etc.,

In order that photoelectric current may adopt the unique way of flowing, it is what can be outputted as a digital signal even if input light is analog light and it is digital light, while being able to use it for the photo conductor for electro photography of a digital recording system -- the conventional PPC (analog optical input) -- business -- even if it uses it for a photo conductor, a high-definition picture with sharp edge is realizable.

[Translation done.]